



TITLE:

# Studies on the Rate of Reaction CH and CO. (III)

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Tab. 3. Influence of contact time.  
(Catalyst: MgO; Reaction temp.: 350°C)

Time sec.	F · A	R	A/F	k <sub>1</sub> /k <sub>2</sub>
18	0.500	0.074	1.13	1.04
24.5	0.482	0.104	1.19	0.94
39	0.400	0.137	0.77	0.68

## 25. Studies on the Rate of Reaction CH<sub>4</sub> and CO<sub>2</sub>. (III)

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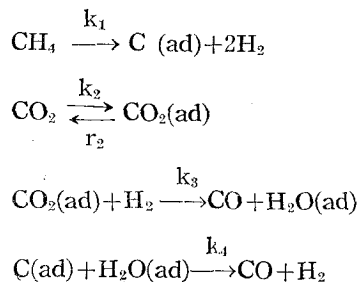
The rate of thermal reaction of CH<sub>4</sub> and CO<sub>2</sub> was investigated at 1147–1236°K and 100–300 mmHg in which the pressure change caused by the reaction was determined and the reaction product was analysed with a modified Ambler's apparatus.

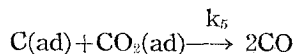
In the earlier stage of the reaction, H<sub>2</sub> is mainly formed, as the result of a mere decomposition of CH<sub>4</sub> and in the later stage CO is formed due to the reaction of CO<sub>2</sub> and H<sub>2</sub> which increased rapidly as the reaction proceeds, but the amounts of CO are always smaller than those of H<sub>2</sub>.

At constant initial pressures of CH<sub>4</sub>, the amounts of H<sub>2</sub> produced are scarcely affected by the initial pressures of CO<sub>2</sub>, but contrarily those of CO change regularly with the initial CO<sub>2</sub> pressure. On the other hand, both amounts of H<sub>2</sub> and CO increase conspicuously with the initial CH<sub>4</sub> pressure when the initial pressures of CO<sub>2</sub> are constant.

In the earlier stage of the reaction, the rate of pressure change is the 1st order with respect to the partial pressure of CH<sub>4</sub>, while the rate of CO formation is always approximately 1st order respecting partial pressure of CO<sub>2</sub>.

On the basis of the results of these experiments and the previous investigations on the rates of the reaction of CO<sub>2</sub>+H<sub>2</sub>=CO+H<sub>2</sub>O and C+CO<sub>2</sub>=2CO, the following mechanism is proposed:





$k$  : velocity constant

(ad): represents the adsorbed state on the reaction vessel surface.

The following equation for the rate of CO formation can be derived from this mechanism with the assumptions that the adsorption of  $CO_2$  exists always in an equilibrium and  $k_5 \ll k_3 \ll k_4$ ,

$$\frac{d[CO]}{dt} = \frac{2 k_2 [H_2]}{r_2/k_3 + [H_2]} [CO_2],$$

which reproduces our experimental results approximately.

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## 26. Syntheses of Antioxidants for Fats and Oils. II

### Cresol-analogs of NDGA and Polynuclear Phenolic Antioxidants

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The two cresol-analogs of NDGA were prepd. The Grignard reagent of p-bromo-o-cresol methylether was condensed with allyl bromide to p-methoxy-m-methylallylbenzene (I),  $b_{42}$  132–142°. The Grignard reagent of the hydrobromide of (I),  $b_{13}$  132–140°, was treated with  $I_2$ , giving meso and racemic mixt. of 1,4-bis(p-methoxy-m-methylphenyl)-2,3-dimethylbutane,  $b_5$  210–215°, meso m. 79–80°. On demethylation with MeMgI and recryst. from benzene, free phenol (II), m. 80–81°, was obtained. p-Cresol allyl ether was rearranged and then methylated to 2-methoxy-5-methylallylbenzene (III),  $b_{45}$  131–132°. Hydrobromide of (III),  $b_{13}$  138–142°, was treated as above, giving 1,4-bis(2-methoxy-5-methylphenyl)-2,3-dimethylbutane,  $b_{2-3}$  195–200°, meso m. 91°, free phenol (IV) m. 163–4°.

The following hindered phenol antioxidants having large molecular size were prepd. The mixt. of 10 g. of 2,6-dimethylol-p-cresol and 39 g. of phenol in 50 ml. of 60% ethanol was saturated with HCl gas at 0°. On standing overnight there resulted white crystals which were filtered and 12 g. of condensate (V), recryst. from acetic acid m. 211–12°, acetate m. 117–18°, was obtained. The determination of the structure is now under way. 2,6-Dimethylol-p-cresol and p-cresol gave crystalline condensate (VI), m. 210–11°, which has probably a four nuclear cyclic structure according to J. B. Niedrel (J. Am. Chem. Soc. **65** 629 (1943)). On similar treatments o-cresol, thymol and eugenol gave amorphous solids (VII), (VIII) and